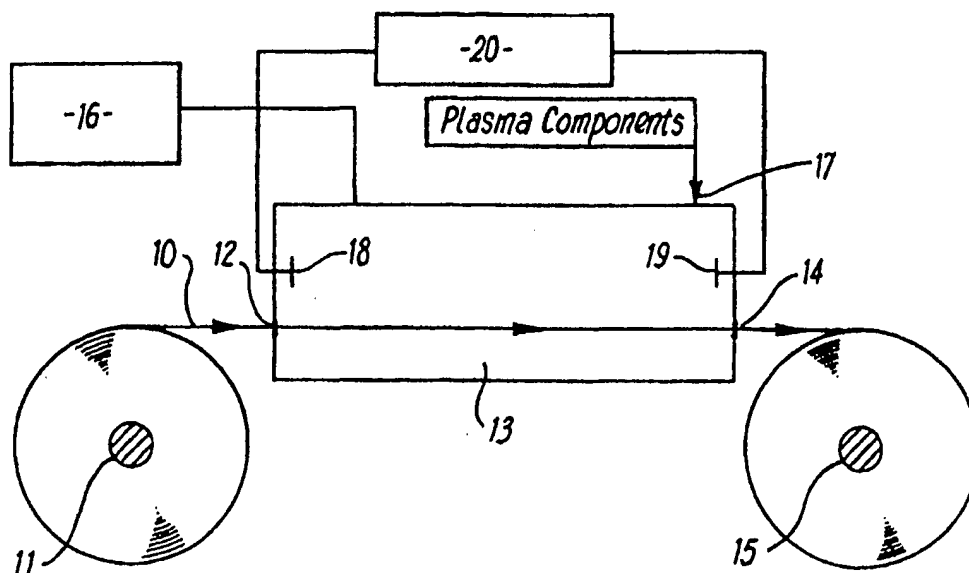




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(54) Title: INDUSTRIAL FABRICS AND METHOD OF TREATMENT



## (57) Abstract

An industrial fabric comprises synthetic yarns or fibres which have been subjected to plasma treatment. If fibres are used, they may be treated as fibres, when made up into yarns or when formed into a woven or nonwoven layer. One or both sides of the layer may be treated. The treatment may enhance hydrophilic properties by using a plasma containing oxygen, air or ammonia. Hydrophilic properties may be enhanced by using a plasma containing a silane, a siloxane or a perfluorocarbon.

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### INDUSTRIAL FABRICS AND METHOD OF TREATMENT

This invention relates to industrial fabrics and to a method of treating such fabrics during the manufacture thereof to impart desired characteristics to the fabric.

5           The invention relates for example to all forms of papermaking machine fabrics including dryer fabrics, press felts, including extended nip press belts, shoe press sleeves, corrugator machine press belts, and also to conveyor belts, printing blankets, silicon wafer grinding belts and filter cloths.

10           These fabrics may be treated for example to influence the wetting characteristics of the fabric, or in a composite fabric of two or more layers, of at least one layer of the fabric. Thus it is known e.g from US 5372876, to provide e.g. a papermaking felt which includes a flow control layer formed of a porous hydrophobic material. Conversely, EP-A-0761872  
15           discloses a dryer fabric having a paper side contact surface which is hydrophilic, to improve adhesion between the paper web and the dryer fabric.

          In both cases, the hydrophilic or hydrophobic properties of the layer or surface are achieved by coating or chemical treatment by application of  
20           the relevant compositions in a liquid medium.

          As a method and means for treating substrates to influence their

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surface characteristics, the technology of plasma treatment is in the process of being developed. A 'plasma' is a fluid state of matter wherein due to excitation, the matter is present in the form of positive and negative ions. Polar molecules may be dissociated into anionic and cationic radicals, whilst  
5 free atoms lose electrons to form free electrons and positively charged atoms - depending upon the degree of excitation, more than one electron may be stripped from atomic shells. Plasmas can exist over an extremely wide range of temperature and pressure; from over atmospheric to near vacuum. Because matter in the plasma exists in the form of charged ions,  
10 the plasma environment is extremely chemically energetic, and it has been proposed to treat the surfaces of materials by exposure to plasmas of selected composition.

It is an object of the present invention to provide fabrics for use in industrial processes, such as in papermaking machines, conveyor belts,  
15 printing blankets and filtration fabrics by way of non-limiting example, which have had surface properties modified by plasma treatment, as an economical and environmentally improved alternative to treatment or coating with a liquid medium.

According to the invention an industrial fabric comprises or includes  
20 a layer or component of synthetic yarns or fibres which have been subjected to plasma treatment.

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From another aspect the invention provides a method of making or preparing an industrial fabric including the step of subjecting at least one surface of a layer or component of the fabric comprised of synthetic yarns or fibres to plasma treatment.

5           The invention also includes apparatus for use in making or preparing an industrial fabric, including a plasma chamber to which material containing synthetic yarns or fibres comprising or for use in making said fabric may be introduced, and removed after treatment.

10           The purpose of the plasma treatment may be to modify the wetting characteristics of the yarn or fibre surface being treated, i.e. to render the surface hydrophobic or hydrophilic.

          Alternatively the yarn or fibre surface is provided with activated sites to improve subsequent coating or dyeing. This treatment may utilise glow discharge dielectric barrier discharge or spray discharge plasma. Compared  
15           with corona discharge treatment techniques the modified characteristics of the treated surface are permanent and far more durable.

          Other characteristics can be enhanced by appropriate choice of composition of the plasma, e.g. improved softness in drying felts especially for tissue making machines, crease resistance and antistatic properties.

20           In a preferred method of the invention, hydrophilic properties are enhanced by subjecting the surface to a plasma comprising or containing

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oxygen, air or ammonia for example.

In another preferred method of the invention, hydrophobic properties are enhanced by subjecting the surface to a plasma comprising or containing a silane, e.g.  $\text{Si}(\text{CH}_3)_4$ , a siloxane, e.g.  $(\text{Si}(\text{OCH}_3)_4)$  or a  
5 perfluorocarbon, e.g. 1-6C perfluoroalkane or tetrafluoroethylene or a combination thereof.

Hard coatings of e.g. carbon may be formed by subjecting the surface to a plasma comprising or containing hydrocarbon e.g. methane. Heat resistant coatings can be applied by using a plasma comprising or containing  
10 halogenated hydrocarbons or unsaturated amines (e.g. tetrachloroethylene; 1,1,2-trichloroethane; allylamine or trichloroethylene). The plasma may be diluted with a diluent gas such as helium.

The synthetic yarn or fibre containing material may be treated in the form of a ready made up layer or web or as fibres or yarns prior to weaving  
15 or making up the layer.

The apparatus may be arranged so that only one surface of a fabric is exposed to plasma treatment.

The apparatus of the invention may comprise means for continuously introducing the material into the plasma chamber, moving the material  
20 through the chamber during treatment, and causing it to leave the chamber after treatment. Alternatively the material may be introduced to the plasma

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chamber in batches, which are subjected to treatment and then removed.

The operating pressure of the plasma chamber may be from in the order of 0.1-3.0 mbar, up to and above 1 atmosphere.

A preferred embodiment of the invention will now be described by way of example, and with reference to the accompanying drawing, which is a diagrammatic view of a plasma treatment machine according to the invention.

In the preferred embodiment, a fabric 10 e.g. a woven or nonwoven web of synthetic yarns or fibres destined to form all or part of an industrial fabric such as a paper machine press felt, dewatering drying or forming belt, is fed from a dispensing station 11. This is shown simply as a feed roll, but would in practice include guide and compensating devices in addition, as is well known in the art. The fabric 10 is introduced through a self-sealing entry slot 12 into a plasma chamber 13, and exits through a similar self-sealing exit slot 14 after passing through the plasma chamber and being subjected to plasma treatment within the chamber. The treated fabric 10 is then taken up on a winding station 15 which is shown as a simple take up roll, but in practice would include such guide and compensating apparatus as is required, as is well known in the art.

The fabric 10 enters and leaves the chamber 13 through self-sealing slots 12 and 14 as the plasma usually operates at a considerable under-

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pressure, often extremely rarified, e.g. 0.1-3.0 mbar; and sometimes contains components which must not be allowed into the ambient.

To achieve plasma conditions, the chamber 13 is evacuated to the required pressure by pump means acting under pressure control 16. The material to form the plasma is introduced at 17, and excitation proceeds by the creation of an intense electrical field between electrodes 18, 19 subject to a controller 20. The plasma is created by ionising the molecules or atoms of the plasma forming material to form ionised radicals, or to provide free electrons and positively charged atoms.

Treatment is achieved by exposing one or both surfaces of the fabric to the plasma within chamber 13.

The composition of the plasma will be selected in accordance with the objective of the treatment. For example, to improve wettability (hydrophilic) properties of a fabric, the plasma may be created from ordinary air, oxygen, ammonia or a mixture of these.

To provide a water-repellant finish (hydrophobic) the plasma may be created from a siloxane or perfluorocarbon compound.

Examples of other properties which may be enhanced by such plasma treatment are softness (oxygen plasma), crease resistance (dipped in DMSO, then exposed to nitrogen plasma); anti-static finish - chloro (chloromethyl) dimethylsilane plasma; oil repellent finishes, improvement of capillarity, dye



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reception, dyeing depth, bleaching, UV-protection and flame retardancy may also be provided for.

The fabric may instead of being fed continuously as illustrated, be placed in the machine in batches, treated and then removed. The fabric  
5 may be placed on a conveyor to be fed through the chamber, or associated with a backing layer when only one surface is to be treated.

The material to be treated may be in the form of synthetic fibres or yarns prior to making up into a woven or nonwoven fabric and such are particularly suited to a conveyor feed, or to batch treatment e.g in mesh  
10 cages which can be introduced to and removed from the plasma chamber.

A hydrophobic (water repellant) fabric may be used as a flow control layer in a papermaking felt of the kind described in US, 5,372,876, whilst a hydrophilic (with enhanced wettability) fabric may be used as a dryer fabric such as described in EP-A-0761872 mentioned above.

15 The term 'fabric' as used above should be interpreted to cover sintered felts, coatings of coated papermaking fabrics, nonwovens and films, spiral link structures, membranes or polymer matrix material and their components prior to making up where appropriate e.g. sintered particles.

The speed of material being fed into the chamber in the illustrated  
20 version may be 5-100 metres per minute. At present working widths are limited to about 2.7 metres. The development of larger machines capable

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of treating greater web widths is hindered by the practical difficulties associated in maintaining a sufficient vacuum in a larger chamber. It is thus often more convenient to treat yarns and fibres or other fabric constituents rather than finished fabrics.

5           A hydrophilic surface for a dryer fabric, as in EP-A-0761872 obtains improved adhesion between the dryer fabric and the paper web. A hydrophobic surface may be desirable for certain dryer fabrics for contaminant release, whilst forming fabrics may be rendered hydrophobic for the same reasons or may be hydrophilic to improve drainage. It is  
10       believed that a very thin film of water is attracted to the surface of the yarns in the fabric providing "lubrication" for water flowing through the interstices of the fabric. Batt staple fibres in press felts can be rendered hydrophilic to make the felts absorb water better initially, improving the conditioning of the felt and thereby reducing start up times. However, a  
15       layer of hydrophobic batt staple fibres (or base cloth yarns) within the felt can form an anti-rewetting or flow control layer, which hinders the return flow to the web of water which has initially been urged into the felt from the paper (as in US 5372876).

          A further possible use of the invention is by plasma treatment of  
20       yarns, fibres, films or membranes used to reinforce polymer matrices to form belts, such as extended nip press belts, shoe press sleeves, press belts

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for corrugator machines, conveyor belts, printing blankets, silicon wafer grinding belts, or carcass stripping belts. The activated groups formed on the reinforcing substrate surfaces improve bonding with the matrix polymer. This is particularly useful for reinforcing a polyurethane matrix with polyester structural members such as yarns, fibres or fabrics (woven, nonwoven spiral link or membrane), the latter having excellent dimensional stability but poor adhesion to polyurethane. Adhesion may be improved by a factor of 2-3. For this purpose ammonia or nitrogen plasmas are preferred. Yarns, fibres, films, membranes or finished fabrics may be treated by plasma according to the invention to provide hydrophobic coatings for filter cloths (especially those used in dust filtration) to improve cake release.

In some cases, only one surface of the fabric is exposed to plasma treatment. This may be used e.g. for a forming fabric which may be rendered hydrophilic on the machine side. This will reduce rewetting of the web between a couch roll and felt pick-up at the end of a forming section by increasing solids content in the web by as much as 1-3%. This can entail a significant cost saving for the papermaker.

Plasma treatment as outlined above has the advantages that the process is solvent free, (including no use of water), very small amounts of the raw materials are required (e.g. 30-100 mg per m<sup>2</sup> fabric); energy

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consumption is low, as no water is used which absorbs heat; labour costs are negligible; as the process can be automated, and the overall cost per unit area of fabric can be very low.

5       The invention is applicable to all industrial fabrics, including conveyor belts and filter cloths, but is mainly directed to all forms of paper machine clothing.

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CLAIMS

1. An industrial fabric comprising or including a layer of component of synthetic yarns or fibres, which have been subjected to plasma treatment.
2. An industrial fabric according to claim 1, wherein said fabric includes  
5 a layer comprised of synthetic yarns or fibres, a surface of which layer has been subjected to plasma treatment.
3. An industrial fabric according to claim 1 or 2, wherein the yarns or fibres subjected to plasma treatment are provided with activated sites to improve subsequent coating or dyeing.
- 10 4. An industrial fabric according to claim 1 or 2, wherein the yarns or fibres have been subjected to a plasma comprising or containing oxygen, air or ammonia.
5. An industrial fabric according to claim 1 or 2, wherein the fibres have been subjected to a plasma comprising or containing silane, siloxane, or a  
15 perfluorocarbon.
6. A fabric according to claim 5, wherein said silane is  $\text{Si}(\text{CH}_3)_4$ .
7. A fabric according to claim 5, wherein said siloxane is  $\text{Si}(\text{OCH}_3)_4$ .
8. A fabric according to claim 5, wherein said perfluorocarbon is 1-6C perfluoroalkane, or tetrafluoroethylene or a combination thereof.
- 20 9. A fabric according to claim 1 or 2, wherein the fibres have been subjected to a plasma comprising or containing a hydrocarbon.

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10. A fabric according to claim 1 or 2, wherein the yarns or fibres have been subjected to a plasma comprising or containing one or more halogenated hydrocarbons or unsaturated amines.
11. A fabric according to any preceding claim, wherein the plasma is  
5 diluted by helium.
12. A method of making or preparing an industrial fabric including the step of subjecting at least one surface of a layer or component of the fabric which comprises or includes synthetic yarns or fibres to plasma treatment.
13. A method according to claim 12, wherein said plasma treatment  
10 provides activated sites to improve subsequent coating or dyeing.
14. A method according to claim 12, wherein the plasma contains oxygen, air or ammonia.
15. A method according to claim 12, wherein the plasma contains a silane, a siloxane, or a perfluorocarbon.
- 15 16. A method according to claim 15, wherein the silane is  $\text{Si}(\text{CH}_3)_4$ .
17. A method according to claim 15, wherein siloxane is  $\text{Si}(\text{OCH}_3)_4$ .
18. A method according to claim 15, wherein the perfluorocarbon is 1-6C perfluoroalkane, tetrachloroethylene, or a combination thereof.
19. A method according to claim 12, wherein the plasma contains a  
20 hydrocarbon.
20. A method according to claim 12, wherein the plasma contains one or

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more halogenated hydrocarbons or unsaturated amines.

21. A method according to any one of claims 12 to 20, wherein the plasma is diluted by helium.

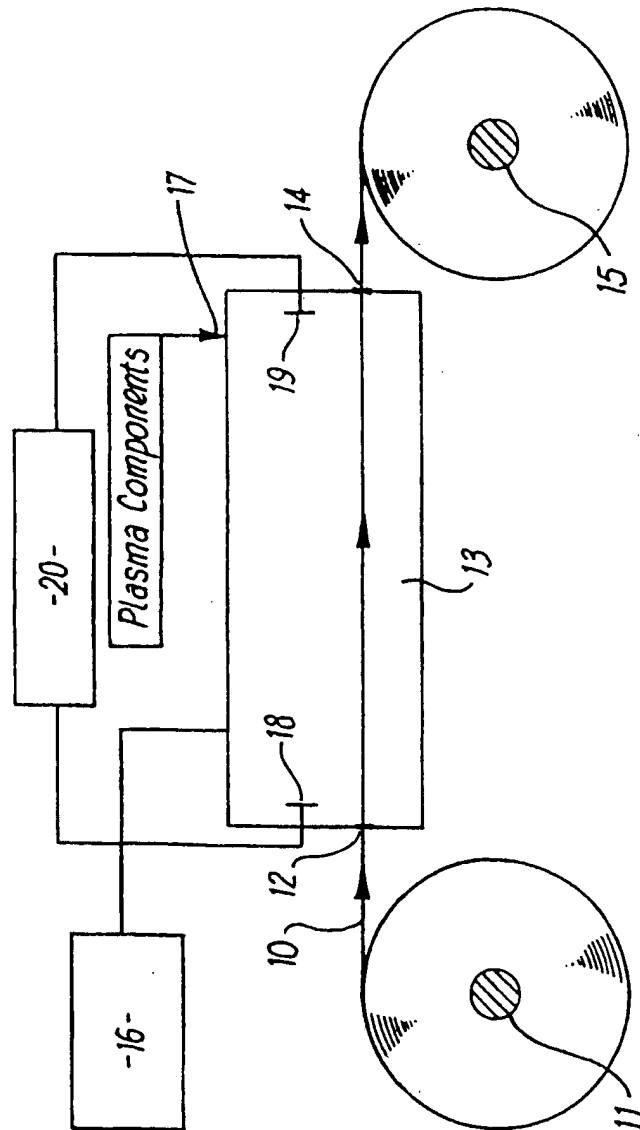
22. Apparatus for use in the method of claim 12, including a plasma  
5 chamber to which material comprising synthetic yarns or fibres forming part of or for use in making a fabric can be introduced and removed after treatment.

23. Apparatus according to claim 22, comprising means for continuously introducing material into the plasma chamber, means for moving the  
10 material through the chamber during treatment, and means for causing the material to leave the chamber after treatment.

24. A fabric or method according to any preceding claim, wherein the synthetic fibres are in the form of yarns to be made up into a woven or nonwoven layer.

25. A fabric or method according to any preceding claim, wherein the synthetic yarns or fibres are in the form of a woven textile layer, at least one surface of which is exposed to plasma treatment.

26. A fabric according to any one of claims 1 to 11, wherein said fabric is, or forms part of, a papermaking machine fabric, an industrial belt or a  
20 filter cloth.



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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/02168

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21F1/00 D06M10/02

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 344 462 A (PASKALOV GEORGY Z ET AL) 6 September 1994	1-4, 12-14, 22, 24-26
Y	see the whole document	5, 7, 9-11, 15, 17, 19-21
X	US 5 041 304 A (KUSANO YUKIHIRO ET AL) 20 August 1991 see the whole document	1, 5, 8, 15, 18
X	EP 0 492 649 A (AMANN & SOEHNE) 1 July 1992 see the whole document	1, 4, 14
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/02168

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 27044 A (MOELNLYCKE AB ;MILDING EBBE (SE); HOLM ULF (SE)) 6 September 1996 see the whole document ---	5,11,15, 21
Y	US 5 622 773 A (REINER ANDREAS ET AL) 22 April 1997 see the whole document -----	7,9,10, 17,19,20

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/02168

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5344462 A	06-09-1994	NONE	
US 5041304 A	20-08-1991	JP 3202145 A	03-09-1991
EP 0492649 A	01-07-1992	DE 4100785 A	02-07-1992
		DE 4100786 A	02-07-1992
		DE 4100787 A	16-07-1992
		AT 141348 T	15-08-1996
		CS 9104081 A	16-09-1992
		DE 59108085 D	19-09-1996
		EP 0496117 A	29-07-1992
WO 9627044 A	06-09-1996	AU 696440 B	10-09-1998
		AU 4893596 A	18-09-1996
		CA 2213809 A	06-09-1996
		CN 1137584 A	11-12-1996
		EP 0833977 A	08-04-1998
		NO 973872 A	22-08-1997
		SE 9500702 A	28-08-1996
US 5622773 A	22-04-1997	CA 2146457 A	16-02-1995
		DE 59400947 D	05-12-1996
		WO 9504854 A	16-02-1995
		EP 0663968 A	26-07-1995
		IL 110454 A	13-07-1997
		JP 8502560 T	19-03-1996